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Evaluation of cast-on-strap joints in lead-acid batteries

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ABSTRACT

The effects of various processing parameters on the lug-strap joint quality of lead-acid auto-batteries are investigated using a laboratory scale cast-on-strap (C.O.S.) set-up. The results indicate that while good quality joints are easily obtained at low cooling rates, at high cooling rate all the C.O.S. parameters such as flux type, strap composition and melt temperature must be carefully controlled to achieve an acceptable joint. Surface treatment with commercially available fluxes, strap melt temperature of 460 °C and strap antimony content of 4.6wt.% Sb render good quality joints at a high strap cooling rate. Furthermore, a dimensionless parameter (relative contact length) for evaluation of lug-strap joint quality is introduced which combines the important lug-strap joint features into a single quantitative parameter and could be used for design of experiments (DOE) and process optimization in the industrial scale.

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1. Introduction

Lead-acid batteries are the oldest and the most widely used type of rechargeable batteries available and still in operation in most automobiles and transport vehicles. They are made up of a number of cells in each alternating positive and negative plates (grids) that are immersed in an acidic electrolytic solution. The electrochemical reactions that take place in the cells produce electrons and the required power for the vehicles.

The cast-on-strap (C.O.S) process is a casting process used for grouping and joining the plates of the same polarity in each cell [1,2]. The joining of the plates is achieved by dipping their lugs into the molten lead alloy of suitable composition which straps them after solidification. Poor lug-strap joint is one of the major manufacturing defects causing early battery failure. The joints provide structural integrity to the cells and act as electrical connections between the individual plates and between the adjacent cells via the inter-cells welds. The joints are therefore required to be mechanically strong, have good resistance to corrosion, and offer low electrical resistance [1]. All of these are linked to formation of a good metallurgical

bond between the lugs and the straps. Formation of any discontinuities like porosity or cracks at the lug-strap interface lowers the strength and increases the electrical resistance of the joints. Such defects also act as corrosion sites and gradually weaken the joints.

In a comprehensive study, Chen et al. [3] characterized the quality of the joints by lack of fusion, partial melting and complete fusion from the strap surface to the lug tip. Lakshmi [1] and Cook et al. [4] have investigated the effects of manufacturing variables on several parameters such as joint meniscus, extent of fusion, gas and shrinkage porosity formation and lug melting. However, almost all of these approaches are qualitative or semi-quantitative in nature and to the best of authors' knowledge, no standard quantitative method has been so far introduced in the literatures for examining the quality of lug-strap joints. Apparently the only practical procedure used in the battery manufacturing industries is random visual inspection and occasional pulling or flipping of the plates to determine whether they are loose. The procedure is highly dependent on the operators' skill and experience as well as their mood, etc.

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In an on-going investigation in one of Iran's largest battery manufacturers, the effects of C.O.S. parameters on the quality of the C.O.S. joints are being investigated. This paper presents the results of some of the preliminary tests carried out in a laboratory scale. The results are presented in terms of a new parameter, i.e. relative contact length (RCL), which combines all the features of the lug-strap joints into a single quantitative parameter. The unique quantitative nature of the parameter makes its application for design of experiments (DOE) and process optimization in the industrial scale possible.

2. Experimental Procedure

2.1. Casting Procedure

A Pb-Sb ingot with 3% Sb, 0.22% Sn, 0.11% As and 0.03% Cu was used in the experiments as the main strap alloy. Four more strap alloys of 4.6, 5.75, 6.75, and 8.5% Sb were also produced by adding suitable amounts of a Pb-Sb master-alloy to the main alloy. Schematics of the laboratory scale cast-on-strap set-up employed are shown in Fig. 1. In each experiment, the required amount of the strap alloy was placed in a stainless steel crucible and melted using a temperature controllable resistance heater (Fig. 1 (a)). The melt temperature was checked with a K-type thermocouple placed in the crucible. At the desired temperature, the crucible was quickly moved to the C.O.S. set-up (Fig. 1 (b)) and the Pb-Ca type lugs of 6 plates grouped according to the battery manufacturer guideline were immersed into the molten strap alloy. Subsequently the melt was allowed to cool and solidify in the crucible to produce the

joints. Three different cooling media, namely air, rammed graphite powder, and water, were used for cooling the crucible in the C.O.S. set-up as shown in Fig. 1 (c) to (e). These provided various cooling rates whose average values are shown in Fig. 1 (c) to (e). The water-cooled crucible provided cooling rates comparable to those experienced in full-scale C.O.S machines. The surface of the lugs were treated by one of the three different commercially available fluxes, namely D05, D07 and DOM, 5 seconds prior to their immersion in the melt to remove the oxide layer on the lugs surfaces.

2.2. Characterization of the Lug-strap Joints

After cooling to room temperature, samples were carefully cut in the middle, ground to 1200 sand paper, polished and etched by a solution made up of 5 parts acetic acid and one part hydrogen peroxide to reveal the main C.O.S. joints characteristics. These included the type of lug-strap meniscus, interface discontinuities such as porosity, fissures or lack of fusion and degree of lug melting.

Researchers have previously studied these features qualitatively or semi-quantitatively [3,4]. In this study attempts were made to combine the most important features of the joints into one numerical output. Therefore a dimensionless parameter named *relative contact length* (RCL) was defined as shown by Eq. (1).

$$RCL = R/I \quad (1)$$

where R , the real contact length between the strap and the lugs, and I , the expected contact length between the strap and the lugs, are defined as following using Fig. 2 as a real example.

$$I = 2L + W \quad (2)$$

$$R = (2L + W + A) - (B + 2M + \sum_{i=1}^n p_i) \quad (3)$$

where W is the initial width and L is the expected immersed length of the lug. A and B are the increase and the decrease in the real contact length, relative to the base line, due to the meniscus type (positive or negative), respectively. p_i denotes the decrease in the real contact length due to formation of a given pore or any other type of volume defects at a lug-strap interface. $\sum_{i=1}^n p_i$ represents the total reduction in the real contact length between the strap and the lugs due to formation of such defects as porosity at the interfaces. Finally, is the length of the tip of the immersed lug melted during COS process. All of these parameters can be easily measured from metallographic images using any image analysis software. Since RCL is a comparative parameter, calibration of the software for length measurement is not even necessary. In this study UTHSCSA Image Tool software was used for the measurements [5].

RCL increases with increase in the quality of the lug-strap joints. A RCL value well below unity represents poor joints between the lugs and the strap. This might be a result of poor wetting between the lugs and the melt, formation of volume defects at the lug-strap interfaces, excessive melting of the lugs, etc. On the other hand, a RCL value close to or greater than unity indicates superior contacts between the strap and the lugs and envisions longer life of the battery. RCL values

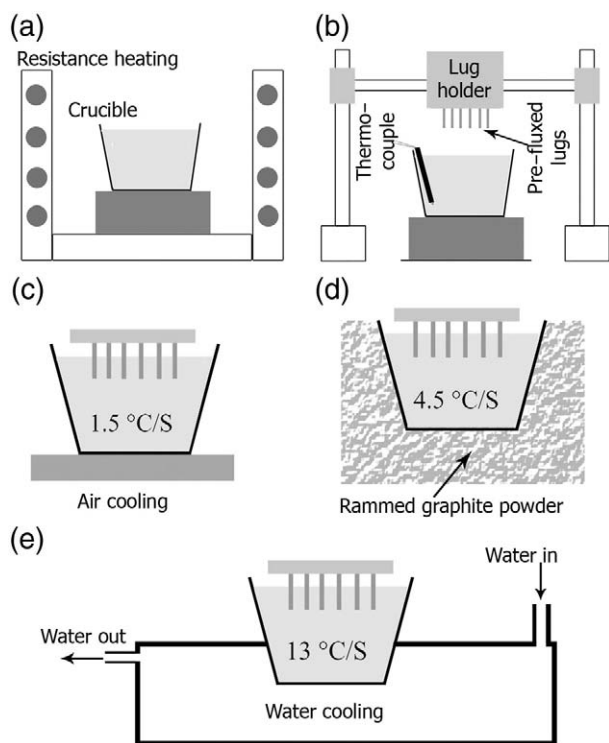


Fig. 1 – Schematic of melting furnace, cast-on-strap set-up and cooling media.

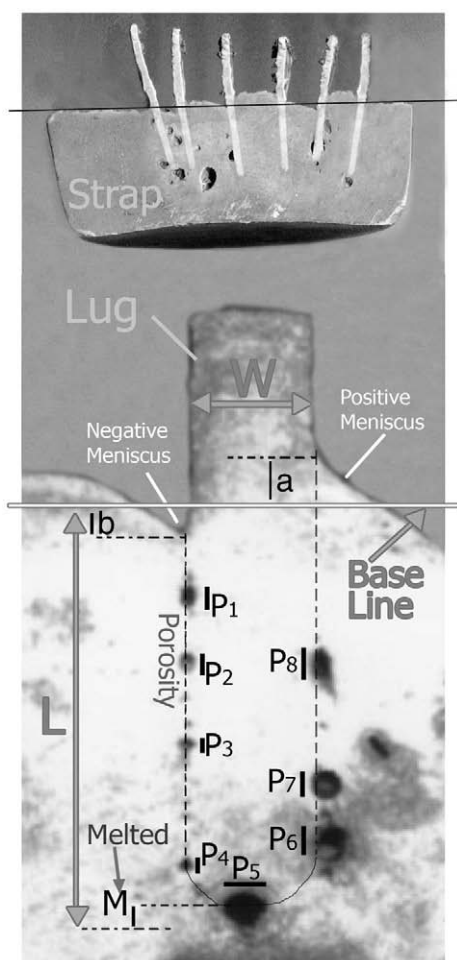


Fig. 2 – Definition of parameters used in calculation of the relative contact length (RCL) of lug-strap joints.

greater than unity is normally plausible when the meniscuses on most sides of the straps are positive and there are little melting of the lugs and little formation of volume defects at the lug-strap interfaces. RCL parameter can be conveniently used for design of experiments (DOE) and process optimization in the industrial scale.

3. Results and Discussion

3.1. Effect of Cooling Rate

Fig. 3a shows the microstructure of lug-strap interface area for an experiment carried out at slow cooling rate (1.5 °C/s) and casing temperature of 460 °C. No sign of porosity, lack of fusion or other types of defects are evident in the figure. In fact, this is a typical microstructure observed in almost all the experiments conducted under different conditions at slow (1.5 °C/s) and moderate (4.5 °C/s) cooling rates. Furthermore, the joint meniscus in all of these samples was positive which indicated high joints qualities. Fig. 3b exhibits the microstructure of lug-strap interface area for an experiment carried out at high cooling rate (13 °C/s) with casing temperature of 460 °C. In contrast to the preceding microstructure, here several joint

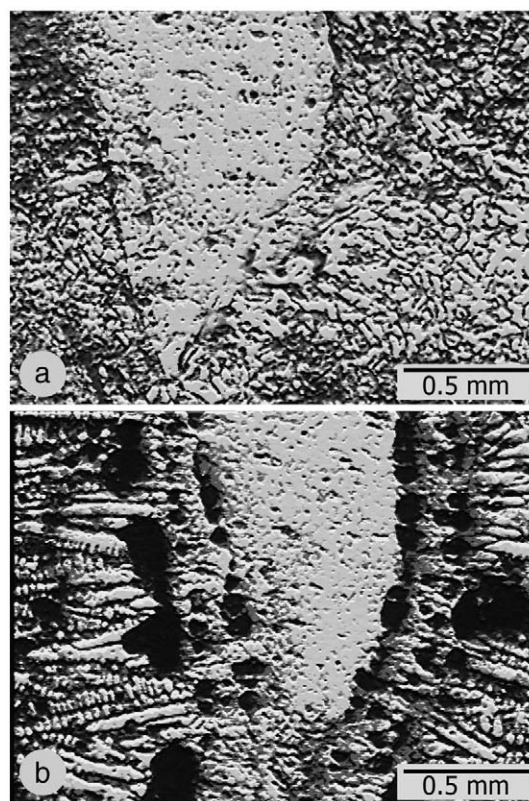


Fig. 3 – Microstructure of lug-strap interface at a) slow cooling rate and b) high cooling rates.

defects are visible. Such defects were observed in many of the experiments carried out at high cooling rate which is close to that encountered in the industrial production. Furthermore, as is shown in Fig. 2, the joint meniscuses for many of lug-strap joints were negative in these experiments.

Fig. 3 also displays the columnar dendritic grain growth of the strap alloy opposite to the direction of heat flow for both slow and high cooling rates. The smaller average primary and secondary arm spacing of the columnar dendrites in Fig. 3b is a result of their higher solidification rate.

Formation of a good lug-strap joint requires good wetting and reasonable fusion between the lug and solidifying strap melt. At the same time there must be enough time available for the escape of the gases formed at the lug-strap interface by vaporization of the thin flux film remained on the lug surfaces. It is believed that at low and moderate cooling rates, sufficient time for wetting, fusion and escape of the gases has been available and therefore high joint qualities have been achieved. On the other hand, microstructural investigations indicated that most defects at the lug-strap interfaces were gas type (as clearly shown in Fig. 3b). Therefore it was concluded that at high cooling rate, the generated gases did not have enough time to escape from the solidifying strap melt and have led to porosity formation at the lug-strap interface.

In the light of the above findings and the fact that mass production speed does not favor the employment of slow cooling rates, the effects of flux type, melt temperature and strap composition on the RCL of lug-strap joints of the

samples processed just by water-cooled mold are presented in the following sections.

3.2. Effect of Flux Type

Table 1 lists the average values of different parameters measured by image analysis for different experiments and used in calculation of RCLs of the experiments.

The purpose of fluxing operation before jointing is to remove or reduce the oxide films formed at the surface of the lugs, and thereby facilitate wetting of the lugs surfaces by molten strap alloy and improve the fusion of lugs surfaces to the strap. It is evident from Table 1 that in experiment no. 4 where the lug surfaces were not treated with any flux, joining between the lugs and the strap were not possible at all. This is also evident from macrostructure of this specimen as shown in Fig. 4.

Commercially available fluxes are acidic solutions of proprietary compositions. Beside their ability to remove the surface oxides, the volume of gas generated during their vaporization and their speed of vaporization are two important factors that affect the lug–strap joint quality. Fluxes that produce less gas are certainly advantageous. However, the optimal speed of vaporization is directly related to the speed of C.O.S. operation. A slower C.O.S. operation would need a flux with slower vaporization. Since the compositions of the fluxes used in this study are unknown to the authors, no comments on their suitability can be made. However, the results presented in Fig. 5 indicate that both DOM and D05 are equally good, while the effect of D07 is significantly lower.

3.3. Effect of Melt Temperature

The effect of strap melt temperature on the quality of cast-on-strap joints is shown in Fig. 6. For the sample cast at 430 °C (the lowest melt temperature), the lugs were all separated from the strap due to the lack of fusion over the entire joints. For a high quality joint, besides the complete wetting of the lug by the molten strap alloy, the lug surface must slightly melt and fuse with the strap alloy. However excessive melting of the lug surface results in smaller contact between the lug and strap (greater M value in Eq. (3)). Fig. 6 shows that the highest relative contact length is achieved at melt temperature of

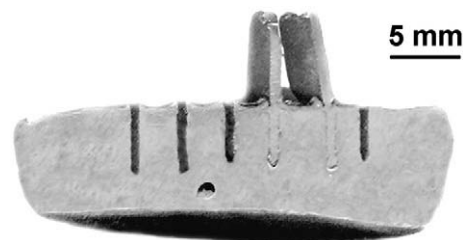


Fig. 4 – Macrostructure of experiment no. 4.

460 °C. Further increase of melt temperature results in excessive melting of lugs and steady decrease of relative contact length between the lugs and the strap.

3.4. Effect of Strap Composition

Fig. 7 displays the influence of antimony content of the strap alloy on the relative contact length of lug–strap joints. It shows that the maximum contact length is obtained at a medium value of antimony content (4.6wt.% Sb). In order to explain this effect, two opposite phenomena should be considered:

(I) For a proper fusion between the lugs and the strap, the lugs surfaces should be completely wetted by the molten strap alloy and sufficient heat should be transferred from the melt to the immersed lugs. This should allow for slight melting of the lugs surfaces. Entrapped gases produced by flux vaporization at the lug–strap interfaces present a barrier to wetting of lugs surfaces and also to efficient heat transfer from the molten strap alloy to the lugs. Previous researches [1,2] have shown that high fluidity and long fluidity life of the molten strap alloy are crucial for minimizing the effects of this barrier. At such conditions lugs are wetted more easily and the generated gases can escape to the melt surface more freely, promoting good lug–strap bonding.

Fig. 8 displays the lead rich part of the non-equilibrium Pb–Sb phase diagram [2] and the relationship between the percentages of the eutectic melt formed during solidification and antimony content of the melt using lever rule. As it is evident from the phase diagram, solidification starts with formation of nearly pure lead dendrites. As the melt temperature decreases, the antimony content of both solid and

Table 1 – Average measured values of different parameters used in calculation of RCL for different experiments.

Experiment	Sb content (%)	Melt temperature (°C)	Flux type	L (mm)	W (mm)	A (mm)	B (mm)	M (mm)	P (mm)
1	3	460	D07	12	1	–	1.6	1.3	2.8
2	3	460	DOM	12	1	1.7	–	1	1.2
3	3	460	D05	12	1	1.5	–	1.3	1.4
4	3	460	None	12	1	*	*	*	*
5	4.6	460	D05	12	1	3.7	–	0.9	0.8
6	5.75	460	D05	12	1	3.9	–	1.9	0.8
7	6.75	460	D05	12	1	3.6	–	2.4	0.7
8	8.5	460	D05	12	1	3.5	–	2.5	0.9
9	3	430	D05	12	1	*	*	*	*
10	3	490	D05	12	1	2.2	–	1.8	1.8
11	3	540	D05	12	1	2.4	–	5	2
12	3	610	D05	12	1	2.4	–	6	2.4

*No measurements were possible because all the lugs were separated from the strap after its solidification.

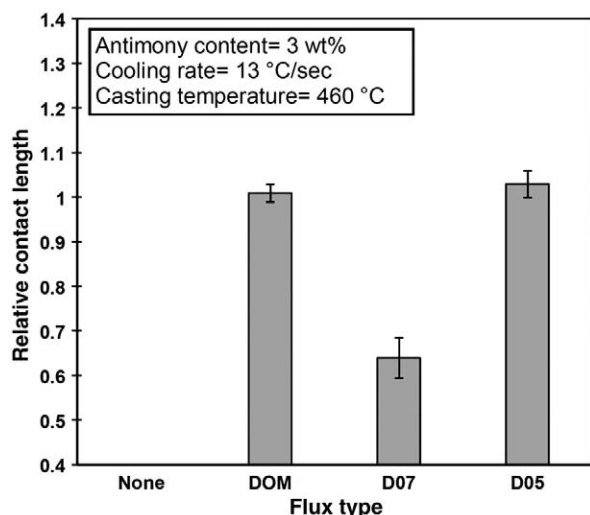


Fig. 5 – Effect of flux type on the relative contact length of lug-strap joints.

remaining liquid counterparts increases. Solidification finishes at 237°C when the last remaining liquid, whose antimony content has reached to 11%, undergoes the eutectic transformation. Fig. 8 shows that the amount of eutectic liquid formed increases by increasing the antimony content of the strap melts. Eutectic liquids are inherently very fluid due to their low melting point and non-mushy mode of solidification [6]. From these considerations, one would expect the lug-strap contact length to increase by increasing the antimony content of the strap alloy.

(II) As the Pb–Sb phase diagram shows, the liquidus temperature of Pb–Sb alloys decreases by increasing the antimony content of the melt. This means that for a given melt temperature, increasing the antimony content of strap alloy is equivalent to increasing the superheat of the strap melt. As discussed in the previous section, this may promote

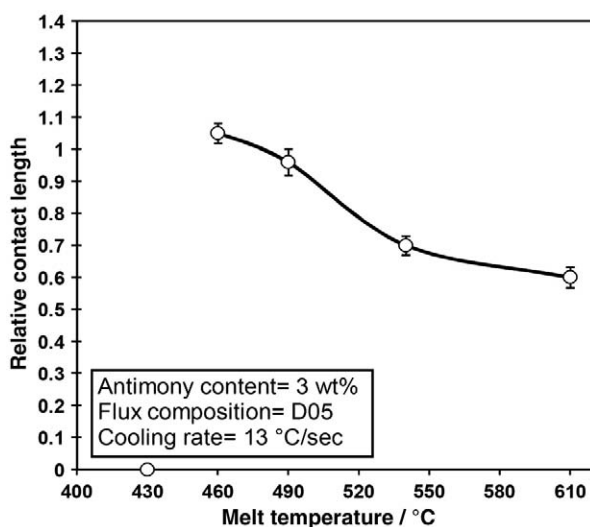


Fig. 6 – Effect of pouring temperature on the relative contact length.

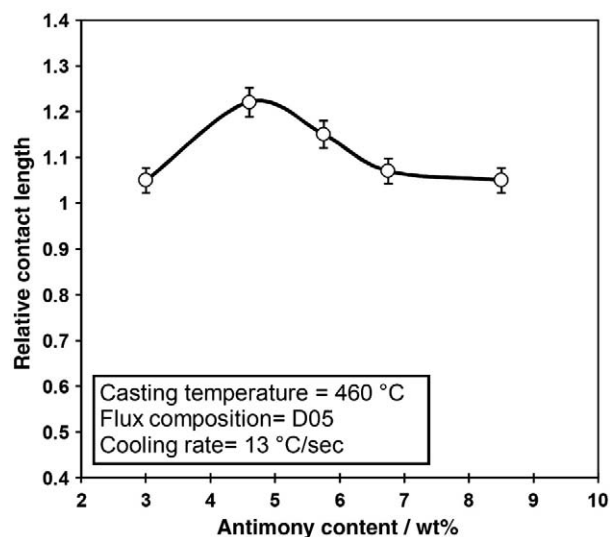


Fig. 7 – Effect of antimony concentration on the relative contact length.

excessive melting of the lugs during solidification of the strap which results in higher M (Eq. (3)) and smaller RCL values.

It seems that the highest RCL value observed at 4.6wt.% Sb is the result of the conflicting effects of these two opposite phenomena.

3.5. Future Work

The results of the preliminary test carried out in a laboratory scale suggested that RCL concept could be a simple but useful way for optimizing the C.O.S. process and provided the incentive for its further utilization. An industrial scale investigation is currently underway for improving the lug-strap joint quality of the C.O.S. processed lead-acid batteries in one of Iran's largest battery manufacturer using RCL concept.

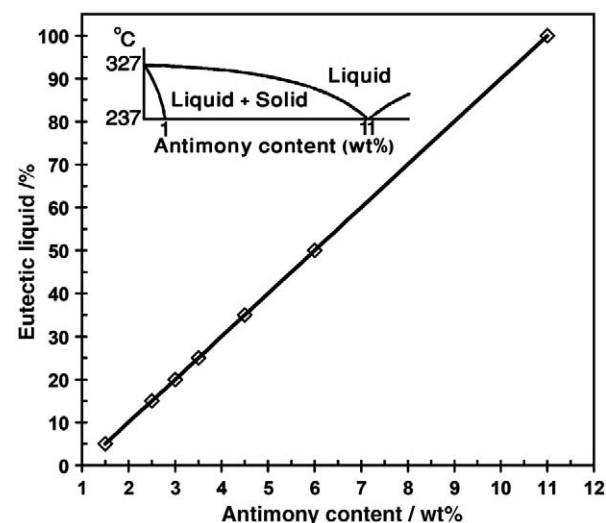


Fig. 8 – Effect of antimony content on the percentage of eutectic liquid formed during solidification of strap alloys calculated from the non-equilibrium Pb–Sb phase diagram (inlay) taken from [2].

4. Conclusions

The preliminary results of an investigation on the effects of various processing parameters on the lug–strap joint quality of lead-acid auto-batteries were presented in this paper. The findings of the study are summarized as following:

- 1- A dimensionless parameter (relative contact length or RCL) for evaluation of lug–strap joint quality was introduced which combines the important lug–strap joint features into a single quantitative parameter.
- 2- Cooling rate during solidification of the strap has an important influence on the quality of the lug–strap joints. Good quality joints are easily obtained at low cooling rates. In contrast, at high cooling rates, practiced in industrial scale production, all the C.O.S. parameters such as flux type, strap composition and melt temperature should be carefully controlled.
- 3- At high strap cooling rate, for straps containing 3wt.% Sb and treated with D05 flux, the best joint quality was achieved at strap melt temperature of 460 °C. No lug–strap fusion at lower melt temperatures and excessive lug melting at higher melt temperatures decrease the relative contact length between the lugs and the strap.
- 4- At high strap cooling rate, melt temperature of 460 °C and with D05 flux treatment, the best joint quality was achieved for straps containing 4.6wt.% Sb. This seems to be the result of the opposing effects of increase in the eutectic liquid formed during solidification and decrease in the

liquidus temperature of the strap alloy by increasing its antimony content.

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